



# DEPARTMENT OF DEFENCE SUPPORT

## MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

### REPORT

**MRL-R-870**

POTASSIUM 4-HYDROXYAMINO-5,7-DINITRO-4,5-DIHYDROBENZOFURAZANIDE  
3-OXIDE, THE FIRST IN A SERIES OF NEW PRIMARY EXPLOSIVES

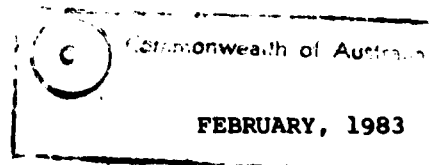
William P. Norris and Robert J. Spear

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ABSTRACT

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The title compound (3) is the first in a series of new structural analogues of the primary explosive KDNEF. (3) readily forms in nearly quantitative yield from reaction of 4,6-dinitrobenzofurazan 1-oxide with hydroxylamine in the presence of  $\text{KHCO}_3/\text{MeOH}$ , and is isolated as free flowing nearly spherical crystals. The sensitivity of (3) to mechanical, electrostatic and thermal stimuli is typical of a primary explosive. Admixtures of (3) with lead azide are extremely sensitive to stab initiation and (3) thus shows excellent promise as a replacement for tetrazene in percussion and stab sensitive compositions. As a single increment, (3) ignites readily but power output is poor and "sooty" ie oxygen deficient.  
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## ABSTRACT

The title compound (3) is the first in a series of new structural analogues of the primary explosive KDNBF. (3) readily forms in nearly quantitative yield from reaction of 4,6-dinitrobenzofurazan 1-oxide with hydroxylamine in the presence of  $\text{KHCO}_3/\text{MeOH}$ , and is isolated as free flowing nearly spherical crystals. The sensitivity of (3) to mechanical, electrostatic and thermal stimuli is typical of a primary explosive. Admixtures of (3) with lead azide are extremely sensitive to stab initiation and (3) thus shows excellent promise as a replacement for tetrazene in percussion and stab sensitive compositions. As a single increment, (3) ignites readily but power output is poor and "sooty" ie oxygen deficient.



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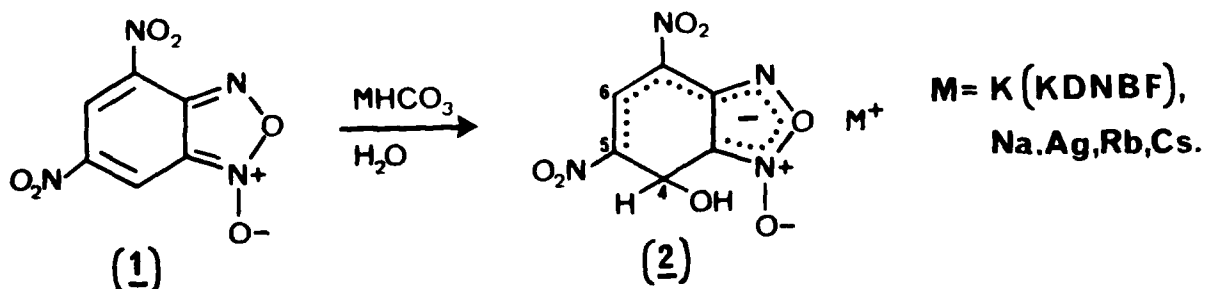
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POTASSIUM 4-HYDROXYAMINO-5,7-DINITRO-4,5-DIHYDRO-  
BENZOFURAZANIDE 3-OXIDE,  
THE FIRST IN A SERIES OF NEW PRIMARY EXPLOSIVES

1. INTRODUCTION

In 1899 Drost prepared a compound to which he ascribed the structure m-dinitro-o-dinitrosobenzene [1]. Uncertainty over the structure of this (and related) compounds was not resolved until the 1960's [2] when it was shown to be 4,6-dinitrobenzofurazan 1-oxide (1)\*, later confirmed by X-ray crystallography [3]. A remarkable property of (1) was that it contained no acidic protons yet dissolved in aqueous alkali bicarbonates to form a series of explosive "salts" [1,4]. Like (1), the structure of these "salts" was not established till many years after their initial isolation when three groups independently showed them to be the Meisenheimer complexes (2) [5,6,7]. The most extensively investigated of these complexes has been the potassium salt, (2,  $M^+ = K^+$ ) known in the explosives literature as KDNEF\*\* [8], which has found use as a primary explosive. The sodium [1,4], silver [1], cesium [4] and rubidium [4] salts have also been reported previously.



\* The common name used in the explosives' literature is dinitrobenzofuroxan.

\*\* The name potassium dinitrobenzofuroxan (hence KDNEF) was used in the pre-1970 literature owing to the fact that the structure was not known. The Chemical Abstracts listing is now under potassium 1,4-dihydro-5,7-dinitrobenzofurazan 3-oxide.

At MRL we are currently involved in an extensive research programme aimed at developing new primary explosive materials. A major part of this programme has been an investigation of structural analogues of KDNBF. If we examine the structure of KDNBF (above), two possible strategies to achieve this are evident.

1. Changing  $M^+$  (from  $K^+$ )
2. Changing the group at C4 (OH in the case of KDNBF), which is derived from the nucleophile which reacts with (1).

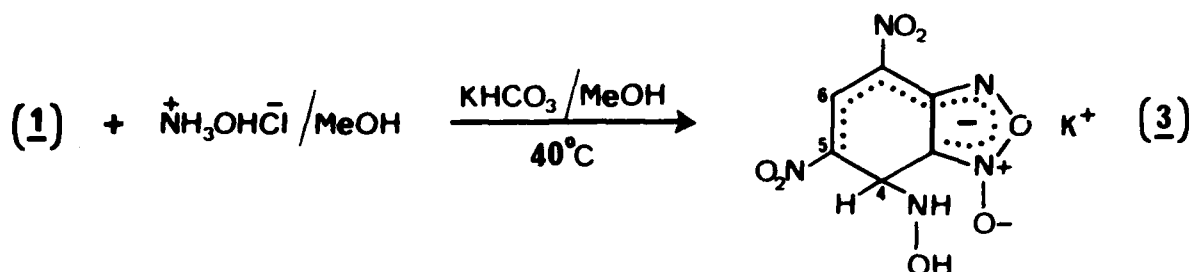
The first strategy is relatively straightforward and a number of such salts are already known [1,4]. We have prepared and examined the sodium, silver and barium salts (2,  $M = Na^+, Ag^+, Ba^{++}$ ) and compared them with KDNBF; an interesting gradation of explosive properties was observed [9]. The alternative strategy is far more challenging since very few compounds of this type have been reported. This is hardly surprising since the structures of neither (1) nor (2) were known for many years. Drost [1] and Gillis and Hoste [4] reported formation of an "ammonium salt" by reaction of (1) with  $NH_3$  in ethanol-benzene and aqueous ammonium ion respectively. Since the determination of the structure of KDNBF, a methoxy derivative has been prepared via reaction of (1) with KOH/methanol [7] and in a very recent study Terrier and co-workers [10] reported spectroscopic observation of complexes between (1) and carbanions from a number of mono- and di-ketones.

We are currently investigating the reaction of (1) with a series of oxygen and nitrogen nucleophiles. A general description of the chemistry and scope of these reactions has been published [11]. The work described here deals with the complex formed by reaction of (1) with hydroxylamine, the first member of this series which we prepared. The preparation and structural proof are detailed, and sensitivity and explosive data are reported.

## 2. SYNTHESIS AND STRUCTURAL PROOF

Addition of a methanolic solution of potassium bicarbonate to a methanolic solution of equimolar amounts of (1) and hydroxyammonium chloride at 40°C resulted in almost immediate precipitation of a dark red material. Inspection by microscopy revealed this product to consist of small nearly spherical crystals which melted, with evolution of gas, beginning at 165°C. The reaction was tried under a number of conditions and five batches, A-E, were prepared. Variation in yield between batches was small (92-100%). When the reaction was carried out at room temperature, where (1) was only partially soluble and dissolved as the reaction proceeded, the product was contaminated by about 1% of unreacted (1) which could be readily seen microscopically as larger yellow crystals amongst the red product crystals. This unreacted material could readily be removed by treatment with chloroform, in which the product was virtually insoluble. The higher temperature reaction is obviously to be preferred since there is no necessity to remove unreacted (1). A further potential benefit was that the reaction at 40°C (Batches A and E) produced spherical free flowing crystals of relatively uniform particle size

whereas the reactions at room temperature produced irregular crystals of a wide variety of particle sizes.

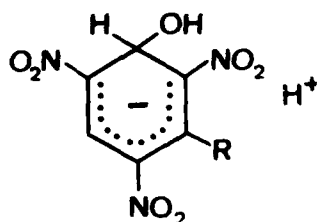
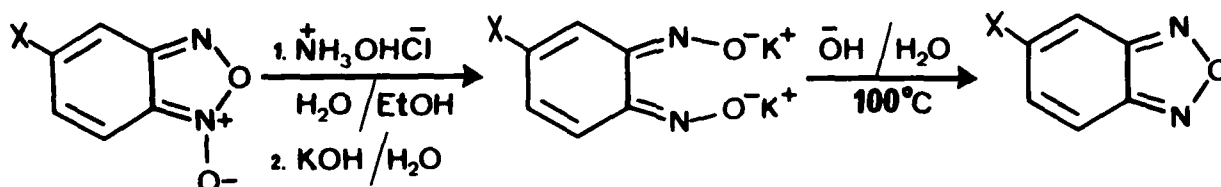


The product of this reaction was readily identified as the Meisenheimer complex potassium 4-hydroxyamino-5,7-dinitro-4,5-dihydro-benzofurazanide 3-oxide (3) on the basis of its correct elemental analysis (C,H,N,K) and spectroscopic data. The UV-visible spectrum in either water or methanol (Table 1) is virtually identical to KDNBF (Table 1) demonstrating that the same chromophore is present. The infrared spectrum, listed in the experimental section, is not particularly informative except for showing the presence both of NH ( $3270\text{ cm}^{-1}$ ) and OH ( $3440\text{ cm}^{-1}$ ) stretches. The lower regions of the spectrum bear a superficial resemblance to that of KDNBF with a number of bands around  $1400$  and  $1600\text{ cm}^{-1}$  resulting from the various N-O stretches, while there is a very strong absorption region from  $1150$ – $1250\text{ cm}^{-1}$  due to a number of overlapping vibrations.

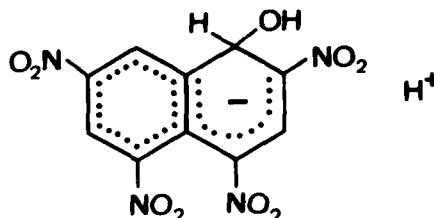
The NMR spectrum (Table 2) conclusively confirms the structure. The spectrum consists of four absorptions of equal intensity, two of which are exchangeable in  $\text{D}_2\text{O}$ . The chemical shifts of the two protons which do not exchange, at  $\delta 8.68$  and  $5.27\text{ ppm}$ , are quite predictable from the corresponding protons in KDNBF (Table 2); the greater deshielding of H4 in KDNBF relative to (3) results from the greater inductive effect of an -OH over an -NHOH group. The two exchangeable protons,  $\delta 7.49$  and  $6.03\text{ ppm}$ , are mutually coupled ( $J = 3.1\text{ Hz}$ ) (the latter proton is also coupled to H4), and are readily assigned to the OH and NH protons of the hydroxyamino group.

The reaction of hydroxylamine with polynitroaromatics can take a number of routes. Meisenheimer [12] observed that reaction with 1,3-dinitrobenzene and 1,3,5-trinitrobenzene resulted in amination of the ring. The intermediate hydroxyamino complexes from these reactions have recently been observed and in some instances isolated [13]. In the case of benzofurazan oxides, reduction to benzofurazans is the reaction normally observed and hydroxylamine is often the reagent of choice to achieve this [2]. In this reduction, hydroxylamine selectively attacks the heterocyclic ring leading to the intermediate dioximo salt which then recycles to the benzofurazan, shown below as Scheme I [2]. Clearly the reaction to (3) is not of this type and again demonstrates the remarkable ability of (1) to form stable Meisenheimer complexes [10, 11]. A quantitative feel for this ability can be obtained from the  $\text{pK}_a$  value for formation of (2,  $\text{M}^+ = \text{H}^+$ ), which is 3.75 at  $25^\circ\text{C}$  [10]. Compare this with the corresponding figures of 13.43, 9.96 and 9.62 for formation of the complexes (4a), (5) and (4b) from the respective nitroaromatics which all would be classified as extremely strong  $\sigma$ -donors [10].

### Scheme I



- (4) a R = H  
b R = NO<sub>2</sub>



(5)

### 3. SENSITIVITY TO INITIATION BY EXTERNAL STIMULAE

(3) was subjected to the standard sensitivity tests for primary explosives: Ball and Disc then Rotter Impact (impact sensitivity), Electric Spark Test (sensitivity to electrostatic initiation) and Temperature of Ignition (T of I, thermal sensitivity). The results are detailed in Table 3; the results for KDNBF [9] are shown for comparison. These tests are designed to assess the susceptibility of an explosive to initiate under such stimuli; sensitivity to friction was not assessed because the appropriate test equipment was not available.

Sensitivity of (3) to mechanical initiation is at a level typical of a primary explosive. The results for the Ball and Disc test, where impact is combined with a pinching action, amply illustrate its high mechanical sensitivity. (3) is thus more sensitive to this test than KDNBF (Table 3). Variations between Batches A-C are small and the relatively narrow range between 100% and 0% ignitions demonstrates predictability and reliability of functioning. The Rotter F of I value, 18, reinforces the assessment of (3) as a sensitive primary explosive. The corresponding figures for lead azide and lead styphnate are 20 and 12 respectively [14].

Both batches which were tested (A and C) ignite in the Electric Spark Test at the lowest test energy, 0.045 J. This complements the impact sensitivity data and is a typical result for a primary explosive. Full electrostatic protection should be observed when handling (3). KDNBF also



ignites at this energy.

In the T of I test, samples of 50 mg are heated at 5°C/min in a test tube. Under these conditions of confinement, (3) deflagrates with a loud bang but in most instances did not shatter the tube. The T of I's were performed in triplicate and show good reproducibility within a single batch but quite wide variation between batches (Table 3). This variation probably results primarily from particle size/shape differences between batches. Batches A and E consist of spherical crystals while the other batches consist of irregular crystals (see Experimental Section). Batches B, C & D were considerably older and we are currently investigating ageing of the samples. Clearly there is considerable scope for production of material with specific crystal habits and properties. For comparison, the T of I for KDNBF is 200°C [9].

#### 4. EXPLOSIVE PROPERTIES

##### 4.1 Stab Initiation

The ability of energetic materials to act as sensitizers in stab (and percussion) sensitive mixtures has been shown to depend significantly on the ignition temperature of the material [15]. The ignition temperatures for (3) (Table 3) are well within the range expected to give a high degree of sensitization [15]. The ability of (3) to function as an energetic sensitizer was assessed on admixtures with lead azide RD1343. Stab initiation energies for 1:10 admixtures (Batches A, B and E) and a 1:20 admixture (Batch E) are listed in Table 4: the corresponding results for tetrazene-lead azide mixtures are listed for comparison. Note that mixing of (3) with lead azide was extremely good with no tendency to separate upon standing. All "fires" upon needle penetration resulted in a detonation and there were no partial ignitions. Stab initiation energies for the admixtures are only twice those for the corresponding tetrazene compositions and well within the range for practical use. Clearly the thermal and hydrolytic stability of (3) would have to be assessed relative to tetrazene but the material obviously shows substantial promise as a replacement for tetrazene in stab (and percussion) sensitive mixes.

The stab sensitivity of a pure compact of (3) was also assessed (Table 4). The 50% initiation energy, 15.5 mJ, demonstrates its high sensitivity. None of the "fires" resulted in an explosion. The normal observation was a flash followed by sooty smoke with virtually no sound output, and the detonator casing was coated with a black residue. In one instance there was a partial ignition where the composition flashed but failed to propagate completely. Microscopic examination of the "no fires" showed no ignited material. The sooty appearance of the output suggests that (3) is oxygen deficient.

## 4.2 Initiation Properties

The explosive properties were investigated to determine whether a confined change of (3) would initiate under normal firing conditions, whether such initiation resulted in a detonation, and whether a sensitive secondary explosive such as RDX could subsequently be induced to detonate. A limited number of experimental detonators were accordingly prepared. The results are detailed in Table 5, entries 1-4.

(3) readily initiates either from match-head igniter (entry 1) or capacitor discharge through a bridgewire (entry 3). Although there was considerable noise output and fragmentation of the detonator tubes, the aluminium witness block was unmarked indicating that buildup to detonation had not been achieved. Initiation of a larger charge of (3) (500 mg, entry 2) again did not result in a detonation. Indeed the poor power output can be gauged from the fact that in neither match-head ignition was the fuzehead bridgewire broken. Firing of a (3)-RDX detonator (entry 4) resulted in unreacted RDX adhering to the undented witness block. This latter result is entirely expected from entries 1-3 above, as well as the results for stab initiation of (3) as a single increment where only deflagration was observed.

## 5. CONCLUSION

4,6-Dinitrobenzofurazan 1-oxide (1) reacts with hydroxylamine in the presence of potassium bicarbonate to form the Meisenheimer complex, isolated as the potassium salt (3). The reaction is nearly quantitative and produces (3) in a pure, free flowing form of small spherical crystals. The sensitivity of (3) to initiation by mechanical, electrostatic and thermal stimuli is typical of a primary explosive and is more than its structural analogue KDNBF. Significant variations in ignition temperature occur between batches. Further investigations of (3) will include reproducibility of sample preparation with respect to crystal size and habit distribution.

Mixing of lead azide with (3), 10:1 by weight, is extremely good and compacts of this admixture are very sensitive to stab initiation. (3) is also quite sensitive to stab initiation as a single increment solid compact but initiation results only in deflagration: the sooty smoke/residue is consistent with oxygen deficiency. When pressed into detonator tubes, (3) ignites readily to explosion either from hot wire or match-head but build-up to detonation is not achieved. A two increment charge of (3)/RDX did not result in ignition of the RDX. In summary, (3) is very sensitive to initiation but has poor power output. The very high sensitization afforded to lead azide shows that (3) has considerable promise as a replacement for tetrazene in stab and percussion sensitive mixes.

Other analogues of KDNBF could be tailored to have a range of explosive properties. This class of materials shows good potential to produce useful energetic materials.

## 6. EXPERIMENTAL

### General

All chemicals used in the syntheses described below were commercially available. Infrared spectra were recorded on a Unicam SP 1000 Spectrophotometer, ultraviolet-visible spectra were recorded on a Varian Superscan 3 UV-Visible Spectrophotometer and NMR spectra were recorded on a JEOL FX-100 Spectrometer operating in the pulsed-FT mode using  $d_6$ -DMSO as solvent. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee, U.S.A.

### 4,6-Dinitrobenzofurazan 1-oxide (1)

4,6-Dinitrobenzofurazan 1-oxide (1) was prepared by nitration of benzofurazan 1-oxide according to the method of Green and Rowe [16]. The crude product was recrystallised from ethyl acetate to give (1) as bright yellow needles, m.p. 173-174.5°C, lit [16] m.p. 172°C. A second crop could be obtained by concentration of the filtrate.

### Potassium 4-hydroxyamino-5,7-dinitro-4,5-dihydrobenzofurazanide 3-oxide (3)

(1) (2.00 g, 8.84 mmol) was added in one portion to a well stirred solution of hydroxyammonium chloride (0.614 g, 8.84 mmol) in methanol (100 ml) at 50°C. Stirring was continued till dissolution was complete (approx. 20 min) then the solution was allowed to cool to 40°C. A solution of potassium bicarbonate in methanol (0.30 M, 59 ml) warmed to about 40°C was then added in one lot; the solution turned deep red and commenced precipitation of a red product almost immediately. Stirring was continued for 30 min at 40°C then the mixture was allowed to cool to room temperature. The product was isolated by filtration under suction, washed with cold methanol (20 ml) and allowed to suck dry at the pump. (3) was obtained as small, almost spherical, free flowing dark red crystals (2.42 g, 91.8% yield), m.p. begins at 165°C with gas evolution. Found: C, 24.24; H, 1.51; N, 23.43; K, 12.93.  $C_6H_4N_5O_7K$  requires C, 24.24; H, 1.36; N, 23.56; K, 13.15. UV, see Table 1; IR (KBr), 3440, 3270, 1630, 1575, 1550, 1440, 1420, 1395, 1230, 1205, 1155, 1080, 820, 740  $cm^{-1}$ ; NMR, see Table 2.

### Experimental Batches of (3)

A number of experimental batches of (3) were prepared to test reproducibility between batches, both for yield of product and variations in response to sensitivity testing. All batches were prepared from 2.00 g of (1) and are referred to in the text as A-E and originate as described below:-

Batch A: 2.42 g, 92%. This was the product whose preparation is detailed above.

- Batch B: 2.46 g, 94%. The reaction was performed at 25°C in methanol (75 ml) and water (75 ml)
- Batch C: 2.46 g, 94%. Same procedure as Batch B.
- Batch D: 2.68 g, 100.0%. Reaction performed at 25°C using only methanol (40 ml) as solvent.
- Batch E: 2.52 g, 96%. Reaction performed as Batch A except sample allowed to cool to 25°C after addition of  $\text{KHCO}_3$ /methanol

#### Sensitivity Tests

Thermal behaviour was initially studied at a heating rate of 10°C/min using a Leitz Ortholux microscope with an attached Mettler FP-2 hot stage, and subsequently by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-2B. Experimental conditions were vented aluminium pans under a flowing nitrogen atmosphere (15 ml/min), heating rate 10°C/min. Ignition temperatures were determined on an instrument built to specifications for the ERDE T of I test. Samples of 50 mg were heated at 5°C/min and measurements were performed in triplicate.

Sensitivity to electrostatic initiation was determined on an instrument built to specification for the Electric Spark Test. Testings were performed at spark energies of 4.5, 0.45 and 0.045 J. Fires/no fires were determined by sound and visual inspection of the sample.

Sensitivity to impact was initially assessed using the Ball and Disc technique on an instrument built to ERDE specifications. Ten samples were tested at each of a number of drop heights to determine 100% fire and no-fire levels. Impact sensitivity was subsequently assessed using a Rotter Apparatus [14]. Samples of 27 mg were tested using a 2 kg weight falling from heights of 40-80 cm over 5 cm intervals. The figure of insensitivity (F of I) was calculated by comparison with RDX (F of I = 80) determined using a 5 kg drop weight.

#### Investigation of Explosive Properties

Lead azide was type RD1343 and was obtained as a single batch (Batch 12) from MFF St. Mary's, NSW.

RDX was an experimental batch of type RD1347 prepared at MRL.

#### Stab Sensitization and Sensitivity

Sensitized mixtures were prepared by initial remote sieving (3) through a 300  $\mu\text{m}$  sieve to break up aggregates and ensure reasonable homogeneity of particle sizes. Explosive compositions were prepared by adding (3) to lead azide RD1343 in the appropriate ratios followed by fold mixing.

Mixing appeared to be adequate with no tendency to separate upon standing. The stab sensitivity of (3) as a single increment was assessed on material which had not been sieved.

#### Preparation of Experimental Stab Detonators

Experimental detonators were prepared in mild steel tubes, 6 mm o.d., 3.2 mm i.d., length 6 mm, prepared from commercially available tubing. A back filling of lead monoxide was first pressed into the tube in two increments using a remotely controlled Pongrass press at a pressure of 560 MPa. The overall column length of lead monoxide was about 4 mm, requiring a mass of 300-310 mg. The experimental composition was then added on top and the unit repressed at 600 MPa. In all cases sufficient composition was added to result in an explosive compact which was visually flat and almost flush with the top of the detonator tube. The masses ranged from ~ 25 mg of pure (3) to ~ 50 mg of the lead azide-(3) mixtures. The experimental detonators differed from conventional stab detonators in that they were not fitted with a closing disc nor spotted with varnish.

#### Determination of Stab Initiation Energies

The experimental set up, consisting of a drop tower test rig fitted with a quick release mechanism, has previously been described in detail [17]. The striker used weighed 14.5 g and the striker body was refitted with a new needle after every test whether or not a fire occurred. The needle, of a similar design to strikers used in fuzes, was silver steel hardened to 650 HV with a 0.08-0.20 mm flat on the tip. In each experiment the striker was released from a pre-set height to impact on the experimental detonator supported in an aluminium holder held in a mild steel base. Each testing was assessed as "fire" or "no fire" by sound and visual inspection of the detonator tubes:- a "no fire" resulted only in an obvious indentation into the compacted explosive. The detonators were not retested after a "no fire" and were destroyed chemically.

Preliminary determinations were conducted at a number of heights to obtain an approximate 50% fire level. The needle height was then varied using regular intervals of approximately 10% of this fire level. A minimum of 25 detonators were tested for each experimental composition. Results were analysed by the Bruceton method [18] and represent the 50% fire level.

#### Initiation and Detonation Properties

Experimental detonators were fired remotely using an 18 V, 0.08 J capacitor discharge firing box which discharged either through a match-head igniter or a platinum bridgewire. The performance of each experimental detonator was assessed by use of an aluminium witness block, with particular importance being placed upon whether a detonation occurred. The dent imparted to a witness block by a detonation has a distinctly cratered appearance with splaying at the edges. The absence of a dent or the presence of a slight indentation which slopes gradually in from the edges indicates that an

explosion has occurred but build-up to detonation has not been achieved. Although largely a qualitative test, depth of dent studies have been used to determine detonator performance and a number of experimental variables which affect the depth have been identified [19].

a. Initiation using Match-head Igniter

Experimental detonators were prepared by pressing weighed amounts of explosive into flat bottom aluminium ICI detonator tubes, 5.57 mm i.d., approximate wall thickness 0.3 mm, using an Eltor press at a pressure of 90.7 MPa. A type E ICI match-head was then crimped into the detonator tube.

b. Initiations using Hot-wire

Experimental detonators were prepared from perspex detonator tubes, 4.12 mm i.d., to which had been fitted a bridgewire device using Eastman 910 adhesive. The bridgewire device was constructed of bakelite with copper terminals across which had been spot welded a 0.038 mm diameter platinum wire. The entire assembly is shown diagrammatically with a more detailed description in ref. [20]. Explosive charges were prepared by pressing weighed amounts of explosive directly into the detonator tubes at 166 MPa using an Eltor press. Where two increments were used, the initiating charge was pressed in first then the secondary charge was added and pressed on top.

7. ACKNOWLEDGEMENTS

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TABLE 1

UV-VISIBLE SPECTROSCOPIC DATA FOR (3) AND KDNBF<sup>a</sup>

| COMPOUND           | SOLVENT          | $\lambda_{\max}$ , nm ( $\epsilon_{\max}$ ) |             |                |              |
|--------------------|------------------|---|-------------|----------------|--------------|
| <u>3</u>           | MeOH             | 466 (31,300)                                | 356 (7,900) | 304.5 (12,300) | 266 (13,400) |
| <u>3</u>           | H <sub>2</sub> O | 468 (26,300)                                | 351 (7,400) | 303 (10,100)   | 264 (13,100) |
| KDNBF <sup>a</sup> | H <sub>2</sub> O | 463 (25,500)                                |             | 302 (8,060)    | 263 (11,200) |

a Data from Ref. 5.

TABLE 2

NMR SPECTROSCOPIC DATA FOR (3) AND KDNBF<sup>a</sup>

| COMPOUND           | SOLVENT                               | SPECTRUM <sup>b</sup>  |
|--------------------|---------------------------------------|--|
| <u>3</u>           | d <sub>6</sub> -DMSO                  | $\delta$ 5.27, d, J = 1.5 Hz, H-4;<br>8.68, s, H-6;<br>7.49, d, J = 3.1, OH;<br>6.03, broad t, NH.                         |
| <u>3</u>           | d <sub>6</sub> -DMSO/D <sub>2</sub> O | $\delta$ 5.27, s, H-4;<br>8.68, s, H-6.  |
| KDNBF <sup>a</sup> | d <sub>6</sub> -DMSO                  | $\delta$ 5.84, dd, J = 8.0, 0.65, H-4;<br>8.59, d, J = 0.65, H-6;<br>6.21, d, J = 8.0, OH (exchanges in D <sub>2</sub> O). |

a Data from Ref. 9.

b Chemical shifts are in ppm ex TMS, coupling constants in Hz.  
s = singlet, d = doublet, t = triplet.



TABLE 3

MECHANICAL, ELECTROSTATIC AND THERMAL SENSITIVITY DATA FOR (3)

| TEST   | RESULT/OBSERVATION   |
|--|--|
| Mechanical Sensitivity<br>Ball and Disc          | Batch A: 8 cm 10/10, 7 cm 9/10, 6 cm 5/10,<br>5 cm 3/10, 4 cm 0/10.<br><br>Batch B: 9 cm 10/10, 8 cm 8/10, 7 cm 9/10,<br>6 cm 4/10, 5 cm 3/10, 4 cm 0/10.<br><br>Batch C: 10 cm 10/10, 9 cm 8/10, 8 cm 7/10,<br>7 cm 6/10, 6 cm 6/10, 5 cm 5/10,<br>4 cm 5/10, 3 cm 0/10.<br><br>KDNBF: 12 cm 10/10, 11 cm 9/10<br>10 cm 4/10, 9 cm 0/10 |
| Rotter Impact                                    | F of I 18 (RDX 80)<br>100 % 80 cm, 0% 40 cm<br>Mean gas volume 14.6 ml   |
| Electrostatic Sensitivity<br>Electric Spark Test | Fires 0.045 J (Batches A and C)<br>KDNBF: Fires 0.045 J  |
| Thermal Sensitivity<br>T of I Test               | Batch A : 135, 136, 136°C<br>Batch B : 151, 152, 152°C All samples<br>Batch C : 142, 142, 142°C deflagrate<br>Batch D : 144, 144, 144°C<br>Batch E : 123, 124, 125°C<br>KDNBF: 199, 200, 201, explodes   |

TABLE 4

STAB INITIATION ENERGIES FOR (3) AND ADMIXTURES WITH LEAD AZIDE

| COMPOSITION                                      | STAB INITIATION ENERGIES (50% LEVEL, mJ)        |
|--|---|
| <u>(3)</u> -Lead Azide RD1343 (1:10)             | 6.5 (Batch A)<br>7.6 (Batch B)<br>7.4 (Batch E) |
| <u>(3)</u> -Lead Azide RD1343 (1:20)             | 9.2 (Batch E)                                   |
| Tetrazene-Lead Azide RD1343 (1:10) <sup>a</sup>  | 3.3   |
| Tetrazene-Lead Azide RD1343 (1:20) <sup>a</sup>  | 3.5   |
| <u>(3)</u> , single increment                    | 15.5 (deflagrates)                              |
| Lead Azide RD1343, single increment <sup>a</sup> | ca. 1000  |

a Data from Ref. 15, shown for comparison

TABLE 5

EXPLOSIVE PROPERTIES OF EXPERIMENTAL DETONATORS CONTAINING (3)

| ENTRY | DETONATOR TUBE/FILLING                                       | INITIATION | RESULT/OBSERVATION <sup>b</sup>                               |
|-------|--|------------|---|
| 1     | Aluminium <sup>a</sup> / <u>(3)</u> (100 mg)                 | Match-head | Tube Fragmented, loud noise output. Witness block not marked. |
| 2     | Aluminium <sup>a</sup> / <u>(3)</u> (500 mg)                 | Match-head | As entry 1.   |
| 3     | Perspex <sup>c</sup> / <u>(3)</u> (50 mg)                    | Hot-wire   | As entry 1.   |
| 4     | Perspex <sup>c</sup> / <u>(3)</u> (100 mg) then RDX (100 mg) | Hot-wire   | As entry 1 - unreacted RDX adhering to witness block.         |

a ICI no. 8 detonator tube, 5.57 mm i.d., pressing pressure 90.7 MPa.

b All witness blocks aluminium.

c 4.12 mm i.d., pressing pressure 166 MPa.

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